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Towards carbon efficient biorefining: Multifunctional mesoporous solid acids obtained from biodiesel production wastes for biomass conversion

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ABSTRACT

Multifunctional mesoporous solid acids were prepared by the sulfonation of carbonized de-oiled seed waste cake (DOWC), a solid waste from biodiesel production. Detailed structural characterization of the materials by elemental analysis, FT-IR, Raman, XRD, XPS, TGA, NH_3-TPD and N_2-physisorption showed that they were structurally different from the carbohydrate and resin based sulfonated carbon catalysts. In addition to the typical —OH, —COOH and —SO_3H groups they contain several N species (pyridinic, pyrrolic etc.) incorporated in their carbon frameworks. The basic structural unit of these materials is a flexible carbon nitride sheet which is extensively functionalized with acidic groups. Our results show distinct effects of raw material composition and preparation methods (activation, sulfonating agent etc.) on structure, stability, surface acidity and textural properties. Here, catalyst —SO_3H density and porosity (pore size, pore volume and surface area) had a direct effect on activity. Also, H_2SO_4 was less useful than 4-BDS (4-benzenediazoniumsulfoante) as a sulfonating agent. The best catalysts with mesoporous structure (average pore diameter 3.9–4.8 nm, pore volume 0.28–0.46 $cm^3\ g^{-1}$) and —SO_3H density (0.70–0.84 $mmol/g_{cat}$) were obtained by 4-BDS sulfonation of chemically activated DOWCs. In contrast, hydrothermal H_2SO_4 sulfonation of DOWC produced a non-porous catalyst with high —SO_3H density while those obtained by H_2SO_4 treatment of activated biomass (AC) had a porous structure with low —SO_3H density (0.19 $mmol/g_{cat}$). Furthermore, the reported catalysts show excellent activity in two reactions of interest in biomass conversion: cellulose saccharification (glucose yield 35–53%) and fatty acid esterification (conversion upto 97%) outperforming H_2SO_4, conventional solid acids (zeolites, ion-exchange resins etc.) as well as sulfonated carbons reported earlier works, confirming their potential as alternative environmentally benign solid catalysts for sustainable, carbon efficient biorefining.

1. Introduction

Due to the growing energy crisis and environmental concerns utilization of renewable resources for the production of fuels and chemicals has recently attracted a lot of attention. Thus the conversion of biomass and the platform molecules derived from it into more sustainable bio-based fuels and chemicals (biorefining), is of great interest. Biofuels such as biodiesel and bioalcohols (bioethanol/biobutanol) are presently considered the best alternatives to fossil based liquid fuels [1]. Vegetable oils, fats and fatty acids are the most common feedstock used for biodiesel production while bioalcohols are produced from starchy as well as lignocellulosic biomass. It is a well accepted fact that next to feedstock, catalyst plays the most important role in any chemical transformation by affecting the overall process economics and product costs. Indeed, catalysis is considered as a key, enabling technology for the development of competitive, carbon efficient biorefineries. The current generation technology for biomass conversion still relies on

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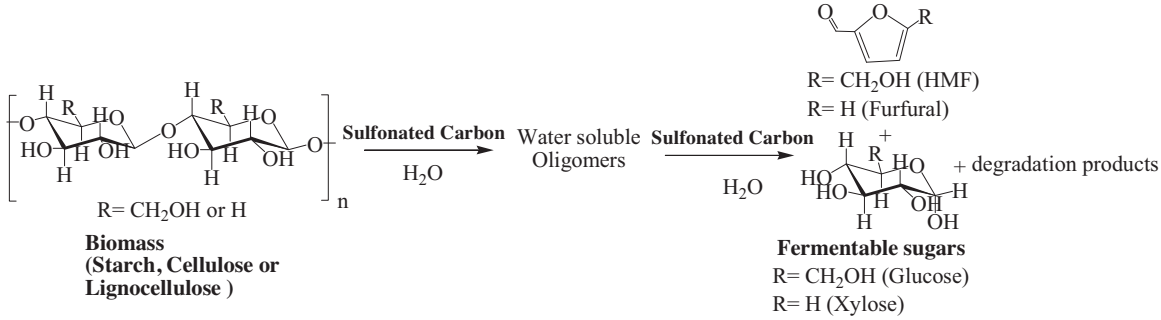
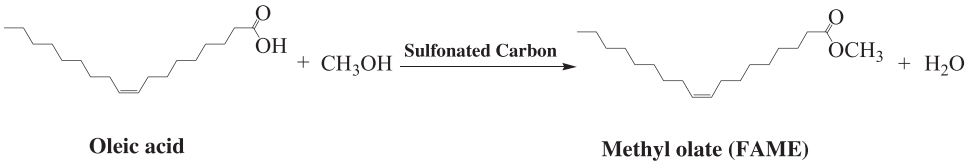
the use of homogenous acids such as HCl, H_2SO_4 as catalyst during many transformation steps, a major hurdle in their large scale commercialization [2]. In recent years, within the emerging concepts of green chemistry use of eco-friendly materials and bio-inspired catalysts for chemical transformations has gained immense attention [3–5]. Among these, the sulfonated carbons have emerged out as promising solid acid and substitute to sulfuric acid. They are a new class of promising, diverse novel solid catalysts active in a range of acid catalyzed reactions including reactions of importance in biomass conversion (biorefining): esterification, transesterification (biodiesel production) [4,5] cellulose saccharification (bioalcohol production and biorefining) [5], glycerol etherification (diesel additive) [6] and to name others. They demonstrate ideal catalytic features such as high mechanical, thermal and chemical stability, water tolerance, activity and low material cost. Over the years, although a large number of manuscripts detailing preparation and applications of these sulfonic acid functionalized materials have been reported. The preparation has been seldom based on a method pioneered by Hara et al. [4] involving sulfonation of an incompletely pyrolysed carbonaceous material obtained from sources such as: sucrose [7], glucose [4,8], starch [9], glycerol [10], biochar [11], wood [12], oil pitch [13], canola meal [14], corncob [15] and to name others. Similar, catalysts have also been prepared from more expensive carbon precursors such as phenolic resins [16], carbon foams [17] graphene [18] and OMCs [19,20]. However, considering that biomass is renewable, abundant and low-cost, sulfonated carbons produced directly from biomass and bio-wastes has potential advantage. In brief, in the majority of studies to obtain sulfonated carbons, the carbon precursors were directly pyrolyzed and treated with strong sulfonating agents (conc. H_2SO_4 or fuming H_2SO_4, except Refs. [17,19,20]) at high temperature. But since the sulfonation step is carried out with large amounts of concentrated acids at a high temperature (150–250 °C), the process may not be reasonably called an eco-friendly. In addition, H_2SO_4 is reported to be ineffective for sulfonating aromatized, ordered and rigid carbon materials such as graphite, activated carbons (AC) or carbons prepared by high temperature treatment [4,5,8,9,14,15]. Hence, by applying the conventional H_2SO_4 sulfonation it is very difficult to sulfonate ACs, in other words to prepare catalysts simultaneously possessing high porosity (large pore size, pore volume, specific surface area) and $-SO_3H$ density, vital features when considering catalytic applications in conversion of large biomass molecules. Recently, it has been demonstrated that sulfonation could be more effective using 4-BDS (4-benzenediazoniumsulfonate radicals) instead of H_2SO_4 due to use of mild conditions, preservation of structural, morphological features of support and the capacity to sulfonate more rigid and ordered carbon structures (AC, graphene, OMC etc.). This approach has been found particularly helpful for sulfonating highly ordered and aromatized carbon materials (e.g., graphene, OMC, AC) and prepare sulfonated carbon catalysts that simultaneously exhibit high porosity and acid exchange capacity. Typically, the porous sulfonated carbon materials are prepared via multi-steps and high-cost strategy, usually involving sulfonation of OMC prepared by a template method [19,20]. In contrast the use of biomass derived porous AC supports for sulfonation is economically more attractive. Although several articles dealing with the preparation of sulfonated carbons from different waste sources could be found in open literature, there are virtually no reports on the employment of end wastes from biodiesel production for making carbon based catalysts. Similarly, studies investigating the effects of preparation method (activation, sulfonating agent etc.), raw material properties on catalyst structure and activity are in lack [17,19,20].

With the growing biodiesel market the use of oil from non-edible seeds such as *Jatropha curcas*, *Ricinus communis* (Castor) and *Pongamia pinnata* has increased in recent years. Oil processing from such seeds generates large quantities of solid wastes in the form of seed hulls and de-oiled waste cake (DOWC). DOWC is an end waste commonly associated with non-edible seeds processing (biodiesel production). Albeit a good source of protein, when obtained from non-edible seeds these cakes do not posses any direct nutritional value as food or fertilize source due to the presence of various anti-nutritional, toxic components (phorbol ester, ricin, karanjin etc.). For the same reason and the low carbohydrate contents they are also not suitable as a feedstock for bioalcohol production or for conversion into manure or direct burning [21–23]. On the other hand, controlled thermochemical conversion of DOWC biomass has been identified to produce high value co-products such as activated carbon (AC), biochar, bio-oil, charcoal for use in the non-food sector [22,23]. Utilization of agricultural residues for preparing AC has already been identified as a cost effective method for waste disposal [24]; extending this concept to the DOWC may be an efficient solution for dealing with these wastes, considering large market opportunities for AC and also from the possible application of such materials during biodiesel production as catalyst, adsorbent for oil,



Scheme 1. Hydrolysis of cellulose/biomass.



Scheme 2. Esterification of oleic acids with methanol.